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Research Article

Fenton Oxidation of Methyl Violet in Aqueous Solution

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In this study, oxidative discoloration of methyl violet (MV) dye in aqueous solution has been studied using Fenton (Fe^{2+}/H_2O_2) process. The parameters such as concentration of Fe^{2+}, H_2O_2, MV, temperature, and Cl^- and SO_4^{2-} ions that affected of discoloration in Fenton process were investigated. The rate of degradation is dependent on initial concentration of Fe^{2+} ion, initial concentration of H_2O_2, and pH of media. Discoloration of MV was increased by increasing the temperature of reaction. Optimized condition was determined and it was found that the obtained efficiency was about 95.5% after 15 minutes of reaction at pH 3. TOC of dye sample, before and after the oxidation process, was determined. TOC removal indicates partial and significant mineralization of MV dye. The results of experiments showed that degradation of MV dye in Fenton oxidation can be described with a pseudo-irst-order kinetic model. The thermodynamic constants of the Fenton oxidation process were evaluated. The results implied that the oxidation process was feasible, spontaneous, and endothermic.

1. Introduction

Wastewaters from textile and dye industries are highly colored. These wastewaters are a large problem for conventional treatment plants in the entire world. Direct discharge of textile industry wastewater into the receiving media causes serious environmental pollution by imparting intensive color and toxicity to the aquatic environment [1]. Methyl violet is a triarylmethane dye, a mutagen and mitotic poison; therefore, concerns exist regarding the ecological impact of the release of methyl violet into the environment. Methyl violet has been used in vast quantities for textile and paper dyeing, and 15% of such dyes produced worldwide are released to the environment in wastewater. Numerous methods have been developed to treat methyl violet pollution. The traditional treatment techniques applied in textile wastewaters, include coagulation/flocculation [2], electrocoagulation [3], ozonation [4], oxidation [5], and adsorption [6–10]. Adsorption only does a phase transfer of the pollutant. The biological treatment is not a complete solution to the problem due to the biological resistance of some dyes [11, 12]; therefore, the resource to advanced oxidation processes (AOPs), like Fenton and photo-Fenton processes, could be a good option to treat and eliminate textile dyes. Homogenous Fenton reaction (Fe^{2+}/H_2O_2) is one of the most important processes to generate hydroxyl radicals $OH^\bullet$ [13–20]. In classic Fenton chemistry, the reaction between hydrogen peroxide and Fe^{2+} in an acidic aqueous solution is generally recognized to produce hydroxyl radicals. The generally accepted free radical chain mechanism for the Fenton reaction is shown as below [21, 22]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^\bullet + OH^- \quad (1)$$

$$OH^\bullet + H_2O_2 \longrightarrow H_2O + HO_2^\bullet \quad (2)$$

$$Fe^{3+} + HO_2^\bullet \longrightarrow Fe^{2+} + H^+ + O_2 \quad (3)$$

$$Fe^{2+} + HO_2^\bullet \longrightarrow Fe^{3+} + HO_2^- \quad (4)$$

$$Fe^{2+} + OH^\bullet \longrightarrow Fe^{3+} + OH^- \quad (5)$$

$$HO_2^\bullet + HO^\bullet \longrightarrow H_2O + O_2 \quad (6)$$

The main objective of this study is to analyze the feasibility of decolorization and mineralization of methyl violet dye by Fenton processes. The influences of different operational parameters (H_2O_2 concentration, Fe^{2+}, MV concentration,

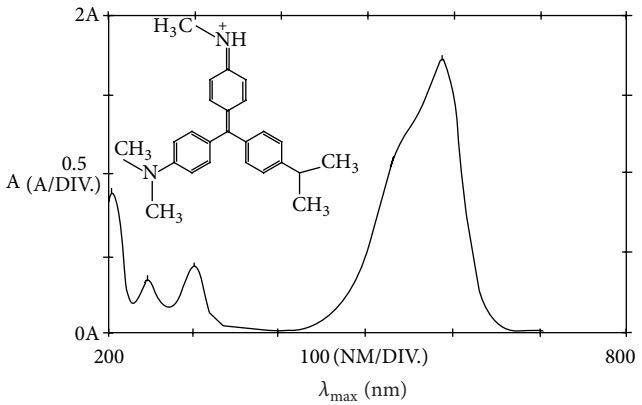

Figure 1: Chemical structure and UV-visible spectrum of MV 3.0×10^{-5} M.

and temperature) which affect the efficiency of Fenton reaction have been investigated. The kinetics and thermodynamic parameters of the process also were determined.

2. Experimental

2.1. Material and Methods. All the reagents used in the experiments were in analytical grade (Merck) and were used without further purification. All the experiments were conducted at room temperature. Methyl violet dye (Tris (4-(dimethylamino)phenyl) methylium chloride, MV, C.I. 42535, MW 393.95) was used as the contaminant. Figure 1 displays the molecular structure and UV-visible spectra of MV dye. 3.0×10^{-5} stock solution of MV was prepared, and working solutions were prepared by the dilution. The dye oxidation was achieved by Fenton's reagent which was composed of a mixture of $FeSO_4 \cdot 7H_2O$ and H_2O_2 30%. The necessary quantities of Fe^{2+} and H_2O_2 were added simultaneously in the dye solution. All experiments were conducted in a 500 mL thermostated batch glass reactor equipped with the magnetic stirrer. The kinetics of oxidation was followed by taking samples at regular time intervals.

The residual concentration of the MV in the solution at different times of sampling was determined. The residual concentration of the dye was deducted from the calibration curves which were produced at wavelength corresponding to the maximum of absorbance (585 nm) on a UV-visible spectrophotometer apparatus (Shimadzu 160 A). The cells used were in quartz 1 cm thick. The discoloration efficiency of the dye (X) with respect to its initial concentration is calculated as

$$\% X = \left([MV]_0 - \frac{[MV]}{[MV]_0} \right) \times 100, \quad (7)$$

where $[MV]_0$ and $[MV]$ are the initial and appropriate concentration of dye at any reactions time t, respectively.

3. Results and Discussion

3.1. Effect of Ferrous Dosage. The concentration of Fe^{2+} is one of the critical parameters in Fenton processes. In the present study, the influence of different iron concentrations ($Fe^{2+} = 1.0 \times 10^{-6}$–$1.0 \times 10^{-3}$ M) is illustrated in Figure 2. The concentration of hydrogen peroxide is fixed a 0.05 M, and dye concentration is 3.0×10^{-5} M. It can be seen from results, MV degradation increased with increasing Fe^{2+} concentrations. This is due to the fact that Fe^{2+} plays a very important role in initiating the decompositions of H_2O_2 to generate the $OH^{\bullet}$ in the Fenton process. When the concentrations of Fe^{2+} and $OH^{\bullet}$ are high, Fe^{2+} can react with the $OH^{\bullet}$ according to (5). The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest $OH^{\bullet}$ radicals production of variable for oxidation [15].

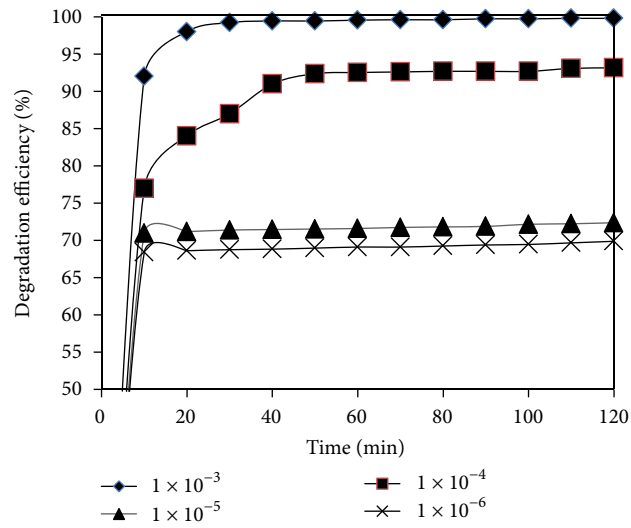

Figure 2: Effect of concentration of Fe^{2+} on the decolorization of MV by Fenton process ($[MV] = 3.0 \times 10^{-5}$ M, $[H_2O_2] = 5.0 \times 10^{-2}$ M).

3.2. Effect of H_2O_2 Concentration. The initial concentration of H_2O_2 plays an important role in the Fenton process. Oxidation of dyes by Fenton process is carried out by $OH^{\bullet}$ radicals that are directly produced from the reaction between H_2O_2 and Fe^{2+}. To determine the concentration of H_2O_2 giving the maximum MV discoloration efficiency, experiments were conducted, and results obtained are represented in Figure 3. The discoloration efficiency according to the time for different concentrations of H_2O_2 shows that the dye degradation yield increases with increasing concentration of H_2O_2. For the Fenton process, the addition of H_2O_2 from 5.0×10^{-3}–1.0×10^{-1} M increases the decolorization from 75% to 90% at 15 min of contact time. The increase in the decolorization is due to the increase in hydroxyl radical concentration by the addition of H_2O_2 [16]. However, at high H_2O_2 concentration, efficiency of dye removal showed no significant efficiency, which is due to the recombination of hydroxyl radicals, and scavenging of OH radicals will occur, which can be expressed by (2) and (6).

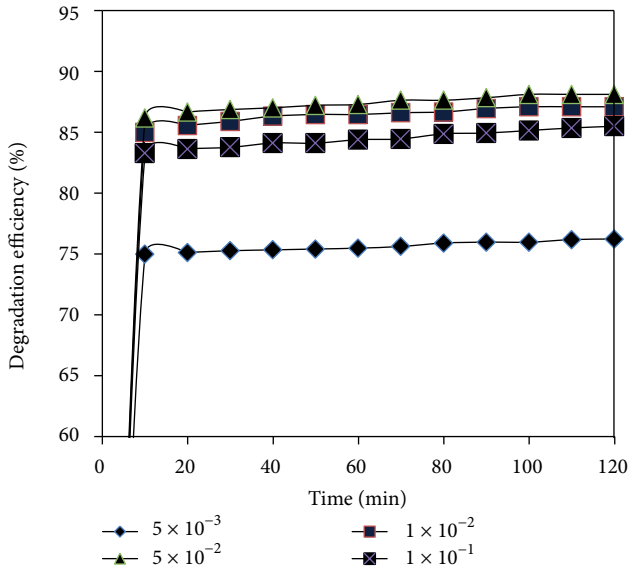

Figure 3: Effect of the of H_2O_2 on the decolorization of MV by Fenton process ([MV] = 2×10^{-5} M, [Fe^{2+}] = 1.0×10^{-4} M).

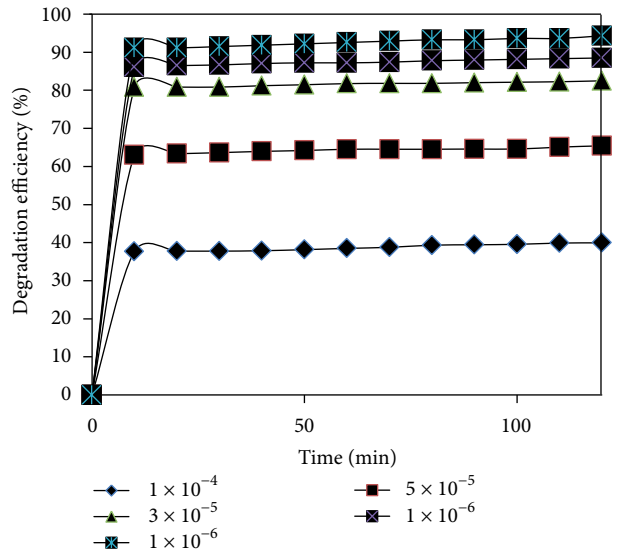

Figure 4: Effect of MV concentration on the decolorization of MV by Fenton process ([Fe^{2+}] = 1.0×10^{-4} M, [H_2O_2] = 5.0×10^{-2} M).

In Fenton process of MV, the decolorization efficiency is not significantly different at the end. More than 70% of the oxidation of MV by Fenton reaction falls down at 15 min of reaction.

3.3. Effect of Ratio of [H_2O_2]/[Fe^{2+}]. To observe the high uptake of dye by Fenton oxidation process, optimal initial [H_2O_2]/[Fe^{2+}] ratio on the degradation of MV dye was investigated. The different ratios (1–400) of [H_2O_2]/[Fe^{2+}] for optimum oxidation of dyes were reported from the literature [23]. The results indicate that the amount of degradation of MV increases when the ratio of [H_2O_2]/[Fe^{2+}] was 5. For bigger value of [H_2O_2]/[Fe^{2+}], it is visible, that the MV degradation decreases. This is due to the fact that at higher H_2O_2 concentration, scavenging of OH radicals will occur, decreasing the MV decolorization.

3.4. Effect of Dye Concentration. The effect of initial concentration of MV dye was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of dye concentration is shown in Figure 4. From the figure, it can be noted that when the initial dye concentration increases, the yield of decolorization decreases [24, 25]. This phenomenon can be explained by the fact that an increase in the initial concentration leads to increasing the number of dye molecules. The number of hydroxyl radicals remains the same. Concentrations of H_2O_2 and Fe^{2+} do not change, which causes a decrease in efficiency of discoloration. When the dye concentration is low, the concentration of H_2O_2 is in excess compared to the latter and traps the $OH^{\bullet}$ radicals. On the other hand, intermediate products increase.

3.5. Effect of Temperature. Temperature affects the reaction between H_2O_2 and Fe^{2+}, and therefore, it should influence the dye degradation. Experiments were performed by varying the temperature from 20°C to 70°C. Figure 5 illustrates the effect of temperature on the reaction of MV discoloration according to time. It may be noted that the temperature has a great effect on the initial rate of MV discoloration. Figure 5 shows that below 15 min, performance is affected by relatively low temperature. After 15 min of reaction, the yield of discoloration is not greatly affected by the temperature in the interval studies. For real wastewater treatment, 35°C to 45°C can be considered as a good range of temperature giving an acceptable performance superior to 80%. Beyond this temperature, there is a slight reduction in yield. The phenomenon may be due to the decomposition of H_2O_2 at relatively high temperatures (8). This is consistent with the results found in the literature [26, 27]

$$2H_2O_2 \longrightarrow H_2O \quad (8)$$

3.6. Effect of pH on Decolorization. The aqueous pH has a major effect on the efficiency of Fenton's treatment. When dye is treated with Fenton's reagent, it may be that the reactant H_2O_2 added might not be sufficiently utilized. This would lead to the residual of H_2O_2 in treated dye waste. Hydrogen peroxide, being a mild oxidant, might affect the subsequent biological process. Thereby residual H_2O_2 was measured.

The reaction was done for 60 min under controlled pH condition with constant dose of Fe^{2+} (1.0×10^{-4} M) and H_2O_2 (5.0×10^{-2} M). It is apparent that the extent of decolorization decreases with the increase in pH, and at pH 3.0 almost >95% color removal was observed (Figure 6). The main reason is that at a low pH more $Fe(OH)^{+}$ is formed, which has much

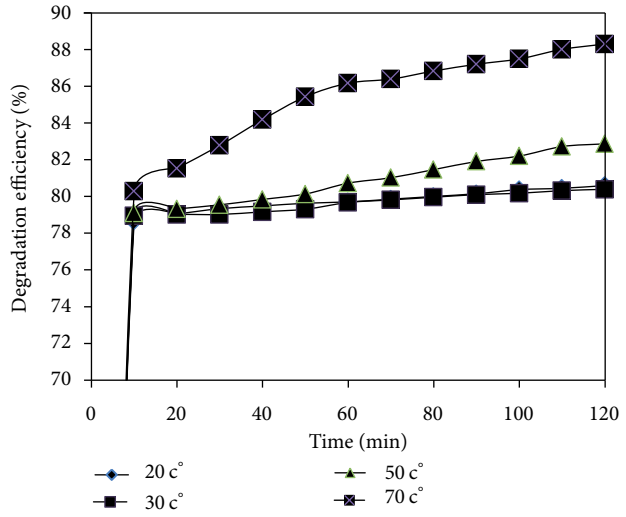

Figure 5: Effect of temperature on the decolorization of MV by Fenton process ([MV] = 3.0×10^{-5} M, [Fe^{2+}] = 1.0×10^{-4} M, [H_2O_2] = 5.0×10^{-2} M).

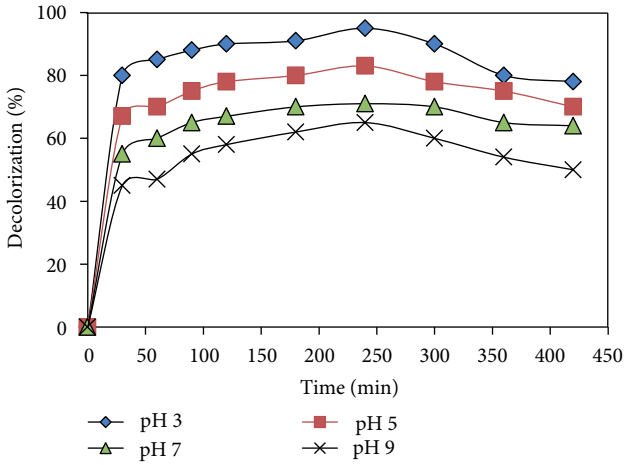

Figure 6: Effect of pH on the decolorization of MV by Fenton process.

higher activity compared to Fe^{2+} in Fenton's oxidation. Also, the generated $OH^{\bullet}$ radicals may be scavenged by the excess H^+ ions [19]. Also at the higher pH, H_2O_2 loses its oxidizing potential. The formation of ferrous and ferric oxyhydroxides under pH values of more than 4.0 inhibits the reaction between Fe^{2+} and H_2O_2. Therefore, the low amount of $OH^{\bullet}$ radical generation can be the reason. Therefore, the pH 3.0 is the optimum pH for Fenton oxidation process [28–31].

3.7. Mineralization Study. It is known that reaction intermediates can form during the oxidation of dyes and some of them could be long-lived and even more toxic than their parent compounds. Therefore, it is necessary to understand the mineralization degree of the dye to evaluate the degradation level applied by Fenton process. Extent of mineralization of

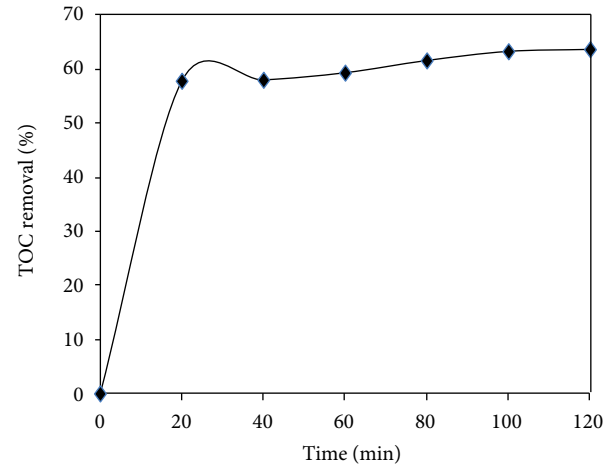

Figure 7: TOC removal of MV dye after Fenton process ([MV] = 3.0×10^{-5} M, [Fe^{2+}] = 1.0×10^{-4} M, [H_2O_2] = 5.0×10^{-2} M).

the dye by Fenton's process can be evaluated by measuring total organic carbon (TOC). To determine the change in the TOC of reaction medium, initial TOC (pure dye solution) and the TOC of a sample at different intervals during the reaction were measured. TOC reduction was determined as follows:

$$\text{TOC}_{\text{removal}} = \frac{(1 - \text{TOC}_t)}{\text{TOC}_0 \times 100}, \quad (9)$$

where TOC_t and TOC_0 (mg L^{-1}) are values at time (t) and at time (0), respectively. 58.5% TOC reduction is achieved for MV dye in 1 h (MV = 3.0×10^{-5}, Fe^{2+} = 1.0×10^{-4}, H_2O_2 = 5.0×10^{-2} M, and pH = 3), which indicates the partial mineralization of dyes [32–34]. Figure 7 shows the TOC removal of MV dye by Fenton oxidation process. The results of TOC removal clearly indicate that the reaction does not go to completion. In fact, after 60 min of reaction, about 58.5% of the initial organic carbon had been transformed into CO_2, which implied the existence of impurity and other organic compounds in the solution. This suggests the presence of residual organic products even after 60 min of reaction, confirming the noticeable degradation of the examined dye.

3.8. Effect of Cl^- and SO_4^{2-} on Fenton Effectiveness. Cl^- and SO_4^{2-} are common coexisting anions with dyes in wastewater; therefore, the effect of Cl^- and SO_4^{2-} ions on MV removal by Fenton process was investigated. It was found that the presence of Cl^- at the concentration range of 0–0.02 mol L^{-1} did not have a significant effect on removing MV. The effect of SO_4^{2-} on the removal of MV was significant at the concentration range of 0–0.001 mol L^{-1}. The removal of MV decreased at a concentration of 0.01 mol L^{-1} of SO_4^{2-}. The removal of MV decreased to 52% for concentration of 0.01 mol L^{-1} of SO_4^{2-}.

4. Conclusion

From the results of Fenton oxidation studies of MV, a model compound of textile wastewaters, the following conclusions can be drawn.

(1) The optimal parameters for Fenton process are

$$[\mathrm{MV}] = 3.0 \times 10^{-5}\ \mathrm{M}, \qquad \left[\mathrm{Fe}^{2+}\right] = 1.0 \times 10^{-4}\ \mathrm{M}, \qquad \left[\mathrm{H_2O_2}\right] = 5.0 \times 10^{-2}\ \mathrm{M}, \quad \mathrm{pH} = 3. \tag{10}$$

(2) Fenton process only complete decolorize MV dye, but also partially mineralize the MV dye.

(3) The rate of Fenton oxidation of MV is first fast (15 min) and then is very slow.

(4) The overall equation of MV degradation and produce of carbon dioxide and nitrate ion is as follows:

$$\mathrm{C_{24}H_{28}N_3^+} + 57\mathrm{H_2O} \longrightarrow 24\mathrm{CO_2} + 142\mathrm{H^+} + 3\mathrm{NO_3^-} + 138\mathrm{e^-}. \tag{11}$$

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